Environmental Science & Technology

Article

pubs.acs.org/est

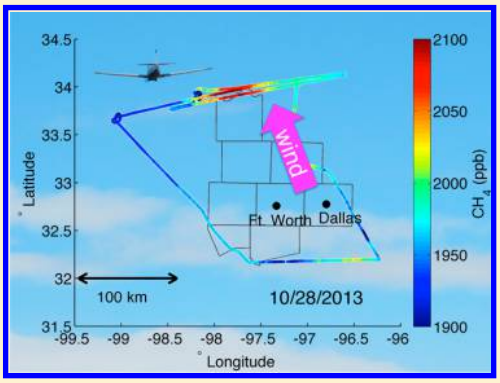
Aircraft-Based Estimate of Total Methane Emissions from the Barnett Shale Region

Anna Karion,*[,†,‡] Colm Sweeney,[†,‡] Eric A. Kort,[§] Paul B. Shepson,[∥] Alan Brewer,[‡] Maria Cambaliza,[∥,△] Stephen A. Conley,[⊥] Ken Davis,[#] Aijun Deng,[#] Mike Hardesty,[†,‡] Scott C. Herndon,[▽] Thomas Lauvaux,[#] Tegan Lavoie,[∥] David Lyon,[○] Tim Newberger,[†,‡] Gabrielle Pétron,[†,‡] Chris Rella,[◆] Mackenzie Smith,[§] Sonja Wolter,[†,‡] Tara I. Yacovitch,[▽] and Pieter Tans[‡]

[†]University of Colorado, CIRES, Boulder, Colorado 80309, United States
[‡]NOAA Earth System Research Laboratory, Boulder 80305, Colorado, United States
[§]University of Michigan, Ann Arbor, Michigan 48109, United States
[∥]Purdue University, West Lafayette, Indiana 47907, United States
[⊥]University of California, Davis, Davis, California 95616, United States
[#]Carbon Now Cast, LLC, State College, Pennsylvania 16803, United States
[▽]Aerodyne Research, Inc., Billerica, Massachusetts 01821, United States
[○]Environmental Defense Fund, Austin, Texas 78701, United States
[◆]Picarro, Inc., Santa Clara, California 95054, United States

Supporting Information

ABSTRACT: We present estimates of regional methane (CH_4) emissions from oil and natural gas operations in the Barnett Shale, Texas, using airborne atmospheric measurements. Using a mass balance approach on eight different flight days in March and October 2013, the total CH_4 emissions for the region are estimated to be $76 \pm 13 \times 10^3$ kg hr^{-1} (equivalent to 0.66 ± 0.11 Tg CH_4 yr^{-1}; 95% confidence interval (CI)). We estimate that $60 \pm 11 \times 10^3$ kg CH_4 hr^{-1} (95% CI) are emitted by natural gas and oil operations, including production, processing, and distribution in the urban areas of Dallas and Fort Worth. This estimate agrees with the U.S. Environmental Protection Agency (EPA) estimate for nationwide CH_4 emissions from the natural gas sector when scaled by natural gas production, but it is higher than emissions reported by the EDGAR inventory or by industry to EPA's Greenhouse Gas Reporting Program. This study is the first to show consistency between mass balance results on so many different days and in two different seasons, enabling better quantification of the related uncertainty. The Barnett is one of the largest production basins in the United States, with 8% of total U.S. natural gas production, and thus, our results represent a crucial step toward determining the greenhouse gas footprint of U.S. onshore natural gas production.



INTRODUCTION

Recent development of horizontal drilling technology and advances in hydraulic fracturing techniques by the oil and gas industry have dramatically increased onshore U.S. natural gas and oil production in the last several years. This production boom has led to widespread interest from the policy and scientific communities in quantifying the climate impact of natural gas as a replacement for coal.[1−3] The primary component of natural gas is methane (CH_4), a powerful greenhouse gas;[4] therefore, natural gas leakage into the atmosphere affects its climate impact.[1,5,6] Improved quantification of CH_4 emissions from natural gas leakage can also help inform understanding of global CH_4 trends.[7−9] Several recent scientific studies have used atmospheric measurements to estimate CH_4 emissions from natural gas and oil operations in different U.S. production basins,[10−17] and on larger regional, continental, and even global scales.[18−21] Other studies have focused on natural gas leakage from transmission and distribution systems in urban areas.[22−24] Nearly all studies have concluded that CH_4 emissions in inventories such as U.S. Environmental Protection Agency (EPA) Greenhouse Gas Inventory[25] or the Emission Database for Global Atmospheric Research (EDGAR)[26] are underestimated compared to

Received: December 10, 2014
Revised: April 1, 2015
Accepted: April 10, 2015
Published: July 7, 2015

DOI: 10.1021/acs.est.5b00217
Environ. Sci. Technol. 2015, 49, 8124−8131

estimates based on atmospheric observations. A recent overview of these and other studies concluded that U.S. emissions from the natural gas and oil sectors are likely 1.25–1.75 times greater than the EPA Greenhouse Gas Inventory.[27] However, the basin-scale studies that were available and considered in that review represented only a small fraction of the total natural gas production in the North America; a more recent study estimated CH_4 emissions from three large basins and concluded that their loss rates were similar to the EPA national estimate.[10] More work is needed to determine total U.S. CH_4 emissions from this sector as operating practices and emission rates have been shown to vary widely in different regions.[13,14,16,17,28]

The Barnett Shale is the oldest shale gas basin in the United States; producers in the Barnett have been using sophisticated horizontal drilling and hydraulic fracturing techniques since the late 1990s. The Barnett is also one of the top five domestic natural gas production basins, producing over 5 billion cubic feet of natural gas per day in 2013,[29] accounting for approximately 8% of the net natural gas produced in the United States in 2013.[30] Production in the Barnett is slowly dropping (from 5.7×10^6 thousand cubic feet (MCF) day^{-1} in 2012 to 5.4×10^6 MCF day^{-1} in 2013), and the rate of new drilling is falling rapidly, with 940 drilling permits issued in 2013, compared to over 4000 issued in 2008,[31] as producers have shifted their focus to newer shale gas plays such as the Marcellus, and to more oil-rich, or "wetter" plays. Some liquid (condensate and oil) production occurs in the Barnett as well, totaling approximately 49 000 barrels (bbl) day^{-1}, approximately 0.6% of U.S. crude oil production.[27,28] The Barnett region also has a history of monitoring for air pollutants by the Texas Commission on Environmental Quality (TCEQ) and emissions from natural gas operations in the area have been the subject of several recent studies.[32−36] In 2013, the Environmental Defense Fund (EDF) launched the Barnett Coordinated Campaign, an effort to use atmospheric measurements from small (component-level) scales up to basin-wide scales to determine the CH_4 emissions from natural gas operations in the Barnett Shale and to help bridge the discrepancy between inventories and top-down estimates. Here, we present results from aircraft-based measurements that quantify basin-wide CH_4 emissions for all sources in the Barnett Shale region. We attribute a portion of total emissions to oil and gas operations using simultaneous observations of ethane, presented in a companion paper.[37] Several additional papers will address different aspects of the Barnett Coordinated Campaign, including the development of a bottom-up regional CH_4 inventory.[38]

EXPERIMENTAL METHODS

From March 25 to April 5, 2013, and again from October 15 to 28, 2013, 12 4−5 h aircraft flights were conducted with an instrumented single-engine Mooney TLS operated and piloted by Scientific Aviation, Inc. in the region surrounding the Barnett Shale (Figure 1). During the October period, a second light aircraft, operated by the Purdue University Airborne Laboratory for Atmospheric Research (ALAR), also conducted flights in the region. Both aircraft flew at altitudes from the ground up to 3000 m above ground level (magl), with most of the flight time spent within the planetary boundary layer (PBL), generally between 400 and 1000 magl. Eight flights on the Mooney, four of which coordinated with ALAR flights, were focused on making measurements in the PBL that could be

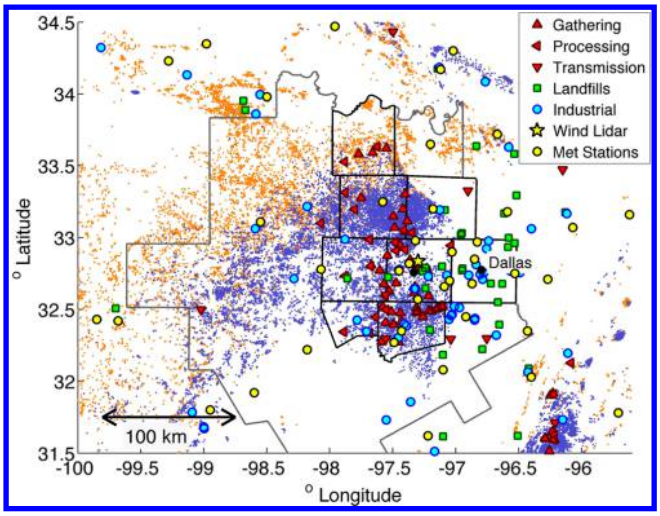


Figure 1. Map of entire region covered by the aircraft flights, with the locations of CH_4 point sources reporting emissions in 2013 to EPA's Greenhouse Gas Reporting Program (GHGRP).[40] Some point source locations were adjusted when they were found to be inaccurate based on satellite imagery. (Orange) Oil and (blue) gas well locations (in October 2013, from DI Desktop[41]) are indicated, as well as (black) the outline of the eight counties that were covered by all eight mass-balance flights, (gray) the outline of the 25-county region defined as the Barnett Shale by the Texas RRC, (yellow ☆) the location of the HRDL (wind Lidar), and (yellow ○) the ground meteorological stations used to nudge the WRF-FDDA model. Wells are considered gas wells if they produced >100 MCF day^{-1} of natural gas per bbl day^{-1} of liquids in October 2013.

used in a mass balance approach to determine total CH_4 emissions (Table 1). Other flights characterized the spatial distribution of both absolute enhancements and enhancement ratios of different trace gases. Ethane, the second largest component of natural gas after CH_4, was used as a tracer for differentiating natural gas emissions from those of other methane sources, such as agriculture or landfills, which do not emit any nonmethane hydrocarbons such as ethane.[39] Ethane measurements and the methods that were used to apportion CH_4 emissions are described briefly in the Results section and presented more thoroughly in Smith et al.[37]

Both the Mooney and ALAR were instrumented with Cavity Ring-Down Spectroscopic (CRDS) analyzers (Picarro G2401-m) for measuring ambient CH_4 mole fractions at approximately 0.5 Hz with an overall uncertainty of 1.4 ppb (see Supporting Information for details). The Mooney aircraft also was instrumented with an ethane (C_2H_6) analyzer (Aerodyne QCL-mini), on all flights except 03252013 (Table 1 and S1), making measurements at 1 Hz.[37,39] Both aircraft logged GPS location and were instrumented to measure horizontal winds, temperature, humidity, and pressure. A ground-based High-Resolution Doppler Lidar (HRDL) was also deployed (Figure 1) by the National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) to retrieve profiles of horizontal winds and to estimate the PBL depth 24 h per day during the period covering five of the eight mass balance flights (Table 1). In addition to the field measurements, the Weather Research Forecast (WRF) model v3.4.1 was used in Four Dimensional Data Assimilation (FDDA) mode using operational meteorological measurements (Figure 1) to improve the simulated dynamics, for both March and October campaign periods.[42−44] The physics configuration, simulation

DOI: 10.1021/acs.est.5b00217
Environ. Sci. Technol. 2015, 49, 8124−8131

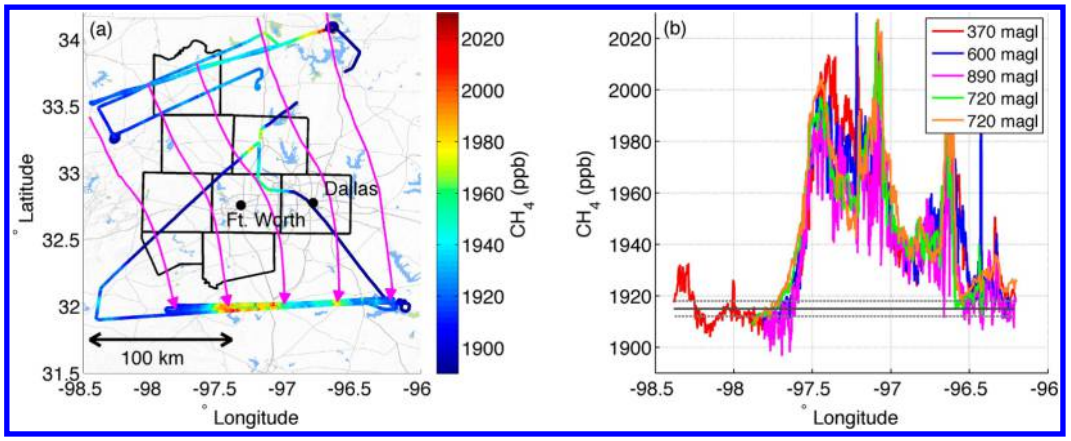


Figure 2. (a) Flight path for mass balance flight 10192013, colored by CH_4 dry air mole fraction, from both aircraft (underlying roadmap from Google). Magenta arrows, pointing in the direction of mean transport, indicate the 10 h trajectories to the downwind transects, constructed using the WRF model winds averaged over time and within the PBL. (b) CH_4 mole fraction in the downwind plume, as sampled along five transects at different flight altitudes between 600 and 1070 masl (370−890 magl). The dark gray line indicates the background at 1915 ppb, estimated using the lateral edges of the plume, with the dashed gray lines indicating its estimated uncertainty (3 ppb). See Supporting Information for uncertainty estimates and flight times.

domain, and details on the HRDL measurements are presented in the Supporting Information.

A mass balance approach was used to estimate the total CH_4 emission in the flight region (Figure 1) on eight individual days, using methods similar to those described in Karion et al.[13] and Pétron et al.[16] In the mass balance approach for flux estimation, the enhancement plume of the CH_4 mole fraction downwind of the source, relative to a background mole fraction, is integrated across the width of the plume in the PBL. When the mean horizontal wind speed and direction are steady during the transit of an air mass across an area, the resulting calculated horizontal flux is equal to the surface emission between the background location and the downwind measurement. This calculation requires the assumption of steady horizontal wind direction, a well-developed convective PBL, and measurements sufficiently downwind of the emission source such that the emissions are vertically distributed throughout the PBL. These conditions were met on all eight of the days used for the mass-balance calculation. Two key differences from the approach of the Karion et al.[13] and Pétron et al.[16] studies are (1) the use of WRF-FDDA reanalysis winds, which account for spatial variability in the horizontal wind field, and (2) the use of a second aircraft to cover the field and allow more flight time in the downwind plume for multiple passes at different flight altitudes (Figure S4, Supporting Information). Details on the application of the mass balance method to these flight measurements are presented in the Supporting Information.

RESULTS

Mass Balance CH_4 Emissions Estimates. Total CH_4 emissions for the region including and surrounding the Barnett Shale (Figure 1) were estimated using a mass balance technique for eight different flights (Figure S3, Supporting Information). Figure 2 illustrates an example of a downwind plume from flight 10192013, sampled on five separate transects at different aircraft altitudes (ranging from 600 to 1070 m above sea level (masl), or ∼370 to 890 magl) between 12:40 pm and 4:00 pm local time (Central Daylight Time, CDT, or UT-5 h) on this day (Table S1, Supporting Information). Multiple transects (which were conducted on 5 of the 8 flights; Figure S4, Supporting Information) illustrate the repeatability of the measurements and the validity of the assumption of uniform CH_4 mole fraction with altitude within the PBL and with time. Flights were conducted under relatively steady wind conditions, with the exception of flight 10202013; on that day, an increase in wind speed over the course of the day resulted in lower mole fractions measured in the plume at higher altitude because it was sampled later in the day (Section 4 and Figure S4, Supporting Information). Results for individual transect calculations are presented in Table S1 (Supporting Information) and show differences between calculations from different transects on the same flight day. Mean horizontal winds for the calculation were derived from the WRF-FDDA model simulated winds and averaged using equal pressure intervals from the surface to the top of the PBL, over the horizontal domain, and over time of transit of an air mass to the downwind transect. These winds were used to calculate bulk transport trajectories from the downwind transect (Figure 2a) and estimate the upwind area of influence for each flight. Both ground-based HRDL and aircraft-based wind measurements were used to evaluate the model winds.[43] An emission rate was calculated using measurements from each transect; the emission rates from all transects on a given flight were averaged to calculate a mean total emission rate for each flight (details can be found in the Supporting Information).

Total CH_4 emission estimates were calculated for eight flights encompassing different wind directions in two seasons: three in March 2013 and five in October 2013 (Table 1). All eight flights were conducted between noon and 6 pm CDT, with steady wind conditions, including a relatively consistent wind direction for the 18 h prior to the flight time. We used back-trajectories constructed using WRF-simulated wind fields (see Supporting Information) from five locations in each downwind transect (Figure 2a) to account for spatial variability in wind speeds and establish approximate lateral boundaries of boundary layer influence for each flight. Each trajectory was constructed using the average PBL wind at the downwind sampling location and time, and integrating the path backward using this mean wind speed and direction, then repeating the process in 20 min intervals until the upwind location was reached. The upwind boundary was either the location of the upwind flight leg, if it existed, or the location of the gas field

DOI: 10.1021/acs.est.5b00217
Environ. Sci. Technol. 2015, 49, 8124−8131

boundary in the upwind direction. These approximate regions of influence were used to establish the total gas and liquids production (production data for October 2013 from DI Desktop[41]) from the area within each flight's area of influence (Figure S6, Supporting Information).

The net gas produced by wells in the area covered by each flight was very similar between the last seven (out of eight) flights, averaging 5.4×10^6 MCF day^{-1}, with only a 10% difference from the highest to the lowest gas production rate (Figure S6, Supporting Information). The first flight, 03252013, covered 24% less gas production than the mean of all the flights because this flight's downwind leg was upwind of a large portion of the wells in Johnson County (Figure S3a, Supporting Information). The consistency in gas production volume from flight to flight is due to each flight's coverage of the core gas production region and processing and other facilities in eight central counties of the Barnett, shown in Figure 1. Although Dallas County has almost no gas or oil production, we include it because it contributes emissions from the natural gas distribution system and other nonfossil emission sources, such as landfills. The eight counties (Dallas, Johnson, Tarrant, Wise, Denton, Parker, Hood, and Montague) covered by every flight, except for 03252013, constitute 83% of gas production in the larger region shown in Figure 1 (5.2×10^6 MCF day^{-1}), or 92% of the gas production from the 25-county area defined by the Texas Railroad Commission (RRC).[31] Liquids (oil and liquid condensate) production covered by each flight varies more substantially, ranging from 2 to 8×10^4 bbl day^{-1} (Figure S6, Supporting Information). Beyond the eight-county region, we define a larger region as the area between 31.5 and 34.5° N and 100 and 95.6° W, shown in Figure 1, which is the largest extent of the aircraft coverage from all flights (see flight tracks in Figure S3, Supporting Information).

While the flights cover this larger region to different extents, flight observations suggest that the vast majority of emissions sampled by all eight mass balance flights originate in the eight-county region identified as the core gas-production area. This spatial distribution of the downwind CH_4 enhancements is observed in the mass balance flights themselves, which indicate that the greatest enhancements occur downwind of the eight-county region. For example, the downwind plume on flight 10192013, sampled in the south of the field, shows that the CH_4 mole fraction in the western portion of the transects (west of the eight-county area, at approximately 97.5–98° W) decreases back to the same value as in the eastern portion, defined as the background value (Figure 2a). The same observation holds true for the other mass-balance flights (Figure S3, Supporting Information).

More evidence of the spatial distribution in regional CH_4 emissions lies in the measurements from survey flight 10172013, conducted by both ALAR and Mooney aircraft between 2 and 6 pm local time (Figure 3). This flight was not used to estimate total emissions using the mass balance technique because of weak horizontal winds in the PBL of ∼1–3 m/s from the east and south, which were variable during the day and within the region. The CH_4 measurements on this day, with a PBL height of 1000 magl, showed that mole fractions of CH_4 were highest over the area east of 97.7° W and west of the city of Dallas. This is the region where gas production is highest. The region to the north and west, where gas production falls off and liquids production is higher, does not show as much enhancement in CH_4. These flight measurements indicate that the largest proportion of CH_4 is emitted

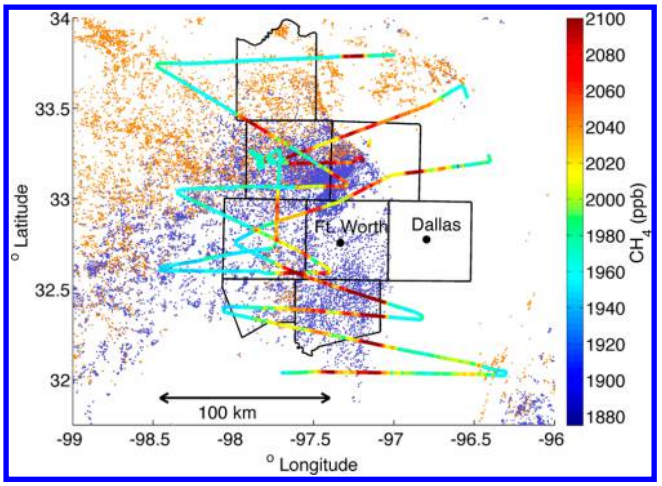


Figure 3. Flight tracks from both ALAR and Mooney aircraft from survey flight 10172013, colored by CH_4 mole fraction (only data within the PBL are shown). The outlines of the eight counties that comprise 92% of the gas production from the 25-county Barnett region are shown for reference, along with the locations of (orange) oil and (blue) gas wells; (black outline) the eight counties that were covered by all eight mass-balance flights.

from the area with the densest concentration of gas-producing wells, and not in the western region where gas production and density of gas wells is lower, but liquids production is greater. On the basis of evidence presented above, we conclude that each flight represents an independent observation of CH_4 emissions coming from the same emissions region encompassed by the eight counties shown in Figures 1 and 3. Thus, the mean of the eight estimates represents the average CH_4 emission rate in this eight-county region.

Although an uncertainty estimate on each day's emissions has been calculated using methods similar to Karion et al.[13] and Pétron et al.[16] (Supporting Information), the reproducibility of the mean emission in this region is derived from the differences between the individual flights. This method treats each day's estimate as an independent estimate of emissions in the region encompassing the eight counties identified. The differences between emissions measured from 1 day to the next can be partly attributed to deviations from this assumption (i.e., to differences in the area of emissions influencing each flight), in addition to uncertainties in the determination of background, variability in horizontal winds, variability in boundary layer height, and variability in actual emissions. We do not expect large temporal variability in emissions from oil and gas production, but there could be some day-to-day variability and/or seasonal variability, especially in nonfossil emissions, such as landfill emissions, that account for some of the variability in our estimates.

Total CH_4 Emission. The eight CH_4 emission estimates are averaged to obtain the total CH_4 emission for the dense gas-production and urban region encompassing the eight counties described above, 76×10^3 kg CH_4 hr^{-1}, with a one-sigma standard deviation of 21×10^3 kg hr^{-1}. Using a statistical bootstrapping method (Supporting Information, Section 8), we determine a 95% confidence interval (CI) of 17% for the mean, or 13×10^3 kg CH_4 hr^{-1} (Table 1).

Table 1 shows the estimated total CH_4 emission rate calculated on each mass-balance flight. The flights were conducted under almost all possible wind directions. Sampling under various wind directions allowed for the elimination of

DOI: 10.1021/acs.est.5b00217
Environ. Sci. Technol. 2015, 49, 8124–8131

Table 1. Summary of Total CH_4 Emission Rate Calculated on Each Mass Balance Flight, the Availability of HRDL and ALAR Measurements on Each Flight, and the Average Wind Direction and Speed[a]

flight date (mmddyyyy)	HRDL	Purdue ALAR	av wind direction[b]	av wind speed ($m\ s^{-1}$)[b]	CH_4 emission rate estimate ($\times 1000\ kg\ hr^{-1}$)
03252013	Y	N	NNW	7.2	78 ± 22
03272013	Y	N	S	11.8	87 ± 18
03302013	Y	N	SW	6.0	78 ± 31
10162013	N	Y	N	7.5	41 ± 8
10192013	N	Y	N	5.6	61 ± 7
10202013	N	Y	S	6.6	88 ± 35
10252013	Y	Y	SE	5.9	109 ± 30
10282013	Y	N	SSE	5.2	64 ± 27
Mean ±95% CI					76 ± 13

[a]Uncertainties reported on each flight's estimate are based on variability in different parameters, such as wind speed and boundary layer height, and from differences between repeated transects on the same day (details in the Supporting Information). [b]Wind speed and wind direction given here are averaged over the domain within the PBL along the flight path of the air mass intercepted in the downwind transects; winds were simulated with the Weather Research Forecast (WRF) model and verified against observations, as described in the Supporting Information and in Lauvaux et al.[43]

bias in the multiday mean due to a possible upwind source when the wind was from a particular direction. In the Barnett Shale, this was a crucial consideration because of its proximity to other oil and gas producing basins, including the Haynesville, Fayetteville, Woodford, and Eagle Ford basins. The multiday average also reduces the effect of other errors that might exist on any one given day (e.g., errors in wind speeds, PBL depth, etc.).

Here, we address several flights that were not ideal for different reasons but were retained in the final analysis. First, the region of influence for flight 10252013 includes a large area farther to the west of the 8-county region but within the 25-county region (Figure S3g, Supporting Information), including 14% more gas production and 4 times more liquids production than the total for the 8 counties. The emissions estimate for this day is 43% higher than the mean of all eight flights, at $109 \times 10^3\ kg\ hr^{-1}$, possibly for this reason. Omitting this flight gives a mean emission rate of $71 \times 10^3\ kg\ CH_4\ hr^{-1}$. Flight 03252013, as discussed previously, did not sample part of Johnson County in the south of the region, thus its influence region included only 80% of the eight counties' gas production. The CH_4 emission rate estimate for this flight is $78 \times 10^3\ kg\ hr^{-1}$, and omitting it makes little difference in the mean, reducing it to $75 \times 10^3\ kg\ hr^{-1}$. Flight 10162013 was conducted on a partly cloudy day, confirmed by satellite images of cloud cover. The conditions may not have been ideal for a mass balance analysis, due to possible increased venting of emissions to the free troposphere (although there was no convection or thunderstorm activity). Flight 10162013 is a low outlier in the emissions estimates, and eliminating it increases the mean emission rate to $81 \times 10^3\ kg\ hr^{-1}$. Eliminating any one of these flights from the analysis does not change the mean emission rate estimate more than our stated 95% CI. While we have investigated the effect of not considering these flights, we have chosen to retain all three, because biases for any given flight cancel in the mean, and imperfections either in the influence region, meteorology, or other unknown factors may exist in other flights as well. We include as many flights as possible in the analysis and use the average as our best emissions estimate. The consideration of eight independent measurements of emissions is the greatest strength of this study.

CH_4 Emissions Attributed to Oil and Gas Operations and Comparison to Inventories. The region surrounding the Barnett Shale includes a variety of CH_4 sources, including oil and gas operations, several large landfills, and some dairy and feedlot operations (there is no evidence in our measurements or in the Global Fire Emissions Database (GFED4, http://www.globalfiredata.org/) of any biomass burning event of significance during either campaign period). In a companion paper,[37] CH_4 and C_2H_6 measurements from the flights are used to derive the proportion of CH_4 enhancement that is attributed to oil and gas operations. In the C_2H_6 analysis, measurements from the survey flight on 10172013 are used to determine how many individual CH_4 plumes show a significant correlation with C_2H_6. Because emissions from biogenic sources do not contain C_2H_6, while oil and gas sources do (including distribution gas in urban areas), the CH_4 to C_2H_6 correlations are used to determine the fraction of CH_4 emissions from nonbiogenic sources. Additional analysis in Smith et al.[37] shows the representativeness of the results from that single flight to the mass-balance flights. The analysis is accomplished using multiple methods, yielding four different results for the fraction of emissions ranging from 71 to 85%, with a mean (±standard deviation) of 79.5 ± 6.0%. Using a similar bootstrap analysis as we did for the total CH_4 emissions and sampling randomly from the distribution of 4 measurements 1000 times gives a 95% CI of (73.5%, 84%). We use this estimate of CH_4 apportionment, propagating the fractional uncertainties, to the total emission estimate to derive the range of CH_4 emissions from oil and gas activities in the Barnett. For comparison, an inventory compiled by Lyon et al.[38] using updated 2013 activity data for the 25-county Barnett area (Figure 1) calculates that oil and natural gas extraction, production, processing, transmission, and distribution contribute approximately 67% of the total CH_4 emission in the 25-county region and 75% in the 8-county core region, an attribution close to the range (73.5−84%) found from the atmospheric analysis presented in Smith et al.[37]

We combine the 95% CI on the fraction of fossil emissions with our 95% CI on the total emissions to estimate a range of oil and gas CH_4 emission of $49–71 \times 10^3\ kg\ hr^{-1}$ (95% CI). For reference, the Lyon et al.[38] inventory estimate for fossil emissions in the greater 25-county region, which is larger than the region covered by most flights (Figure 1), is $42.1–56.4 \times 10^3\ kg\ hr^{-1}$ (95% CI); their inventory estimate for the 8-county core region is $31.4–42.7 \times 10^3\ kg\ hr^{-1}$ (95% CI). The EPA's GHGRP[40] requires large onshore oil and gas producers whose estimated annual emissions exceed 25 000 t CO_2 equivalent to report basin-wide estimates of annual greenhouse gas emissions from natural gas and oil production. Facilities with emissions exceeding the same limit also must report. In 2013, large producers in the three Basins that cover our region of interest (Fort Worth Syncline, Strawn, and Bend Arch) reported combined CH_4 emissions (from production, point sources, and local distribution) of 4 million metric tons CO_2 equivalent for the year 2013, translating to CH_4 emissions of $18 \times 10^3\ kg\ hr^{-1}$, significantly lower than both our estimate and the Lyon et al.[38] inventory. The GHGRP Basins cover a larger area than the 25-county area, and the distribution sector reporting is for the

DOI: 10.1021/acs.est.5b00217
Environ. Sci. Technol. 2015, 49, 8124−8131

entire state of Texas, and we have not scaled the estimates down to our region, so they are an overestimate of the actual reported emissions for the study region. We also note that the GHGRP data have not been scaled to account for producers and facilities not required to report to the program; the producers that report represent 90% of gas production and 88% of energy production in the Barnett. The EDGAR 4.2 inventory[26] for the latest year available, 2010, reported total anthropogenic CH_4 emissions (i.e., including landfills, agricultural, and natural gas and oil emissions) of 43×10^3 kg hr^{-1} (annual average) for the region including the eight counties identified here (between 98.2 and 96° W and 32 and 34° N), also significantly lower than the total emissions we report here ($76 \pm 13 \times 10^3$ kg hr^{-1}). Oil and gas constitute only 12×10^3 kg hr^{-1} in the EDGAR inventory, or 28%, suggesting a more severe underestimate of oil and gas operations emissions in this commonly used inventory.

DISCUSSION

Aircraft measurements over the Barnett Shale have been used to estimate that the total CH_4 emission from a region encompassing the dry gas production region and the urban area of Dallas/Ft. Worth is $76 \pm 13 \times 10^3$ kg CH_4 hr^{-1} (95% CI). The unique strength of this study is the relatively large number of individual flights over two seasons and different wind directions used to derive a robust average estimate of total CH_4 emissions in the Barnett Shale with a low uncertainty. In contrast to previous similar studies,[10,13,16] we have been able to use multiple flight days to obtain a more reliable estimate of average emissions over the entire time period, one that is more representative of average emissions than any measurement conducted over only 1 or 2 days. However, to be able to calculate a more robust annual average, and to assess seasonality in emissions, measurements would be required throughout the year. We note that the partitioning of our total CH_4 emissions estimate into biogenic and fossil emissions relies on analysis from only a single flight, and we make the assumption that this partitioning does not change in time. Conducting more survey flights focused on partitioning CH_4 emissions using co-emitted tracers, such as ethane, would be beneficial in determining how variable different sources are. Conducting this type of study in the same location over multiple years would also allow for the detection of changes in total emissions caused by implementation of emissions reduction strategies or changes in practices.

A second strength of this study is the coordination with a ground-based effort that resulted in the construction of a CH_4 emissions inventory that is concurrent in time with the measurements and thus can be directly compared with the estimate from atmospheric measurements. Our top-down estimate of CH_4 emissions from oil and gas operations in the region, $60 \pm 11 \times 10^3$ kg CH_4 hr^{-1}, (which includes production, gathering, processing, transmission, distribution, and consumption of natural gas and other sources of fossil CH_4), overlaps with the Lyon et al.[38] inventory for comparable sources in the 25-county region ($42.1-56.4 \times 10^3$ kg CH_4 hr^{-1}, 95% CI). Our central top-down estimate is 60% larger than their central estimate for the 8-county region where most gas production occurs ($31.4-42.7 \times 10^3$ kg CH_4 hr^{-1}, 95% CI).

Given the mean gas production covered by the eight mass balance flights' estimated upwind areas of influence, 5.4×10^6 MCF day^{-1} (5.2×10^6 MCF day^{-1}, or 96% of this, is produced in the eight-county area sampled by 7 of the 8 flights), we estimate 3.9×10^6 kg CH_4 produced per hour, assuming the average composition of natural gas produced to be 89% CH_4 by volume (the regional average gas composition[36]) and converting to mass units using industry standard temperature and pressure conditions (15.6 °C and 101.3 kPa). The emissions rate based on our atmospheric measurements from this study region amounts to 1.3−1.9% of total CH_4 production. This percentage is the total CH_4 emission for the Barnett region attributed to fossil sources normalized to CH_4 production in the Barnett region, and caution must be taken when comparing with other definitions of leak or loss rates. We also note that this study does not provide any evidence that CH_4 emission from oil and natural gas operations is a function of gas production volume.

Our top-down final emissions estimate is lower per unit of natural gas produced (1.3−1.9%) than has been found in several previous airborne studies of other oil and gas basins, which found CH_4 emissions ranging from 4 to 17% of CH_4 production;[13,14,16] this study's estimate is closer to the nationwide leakage rate based on the U.S. EPA's inventory for annual natural gas emissions from all components of the gas production chain of approximately 1.5% of production.[25] Indeed, we show that the CH_4 emission rate from oil and gas activities in the Barnett ($60 \pm 11 \times 10^3$ kg hr^{-1}) is comparable to emissions in the Uintah Basin[13] ($55 \pm 15 \times 10^3$ kg CH_4 hr^{-1}), while gas production in Uintah was nearly 7 times lower than in the Barnett (0.8×10^6 MCF day^{-1} in Uintah County vs 5.4×10^6 MCF day^{-1} in the Barnett). However, the current results for the Barnett region indicate that the EPA's GHGRP, which relies on self-reported data only from large producers and facilities, significantly underestimates (by a factor of 3) total natural gas and petroleum associated emissions from the Barnett. We also find that the globally gridded EDGAR inventory underestimates emissions from the oil and gas sector in this geographic region by a factor of almost 5, indicating that it should be used with great caution for the oil and gas sector.

This study covers emissions from all aspects of the natural gas and oil production chain in the Barnett region, and we do not attribute emissions to any particular portion of the production chain, such as drilling or hydraulic fracturing. New drilling in this basin is on the decline, and production is not growing, in contrast to other high-producing basins that are undergoing rapid growth.[31] Further work is required to determine the reasons behind lower CH_4 emission rate per unit of natural gas produced in the Barnett Shale basin compared to many other basins that have been studied so far.

ASSOCIATED CONTENT

Supporting Information

Text sections, table, and figures as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: Anna.Karion@noaa.gov. Phone: (303) 497-6668. Fax: (303) 497-6290.

Present Address

[Δ]Ateneo de Manila University, Quezon City, Philippines

DOI: 10.1021/acs.est.5b00217
Environ. Sci. Technol. 2015, 49, 8124−8131

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was sponsored by the Environmental Defense Fund (EDF) under project code 0146-101000. We thank Robert Harriss and Ramon Alvarez (EDF) for campaign organization and assistance with the manuscript, and the National Weather Service for daily flight forecasts. We thank Jack Higgs, Eric Moglia, Jonathan Kofler, Patricia Lang, Ed Dlugokencky, Duane Kitzis, and Molly Crotwell (NOAA/ESRL/GMD) for their assistance with equipment and calibrations, and Brian Gaudet (Penn State) for assistance with WRF model evaluation. We thank the AirWaterGas Sustainability Research Network, funded by the National Science Foundation, under Grant No. CBET-1240584, for providing one of the CRDS analyzers used in the study. We also thank all the members of the EDF Barnett Coordinated Campaign science team for their assistance in the field and valuable workshop discussions.

■ REFERENCES

(1) Newell, R. G.; Raimi, D. Implications of shale gas development for climate change. *Environ. Sci. Technol.* **2014**, *48* (15), 8360−8368.

(2) Weber, C. L.; Clavin, C. Life cycle carbon footprint of shale gas: Review of evidence and implications. *Environ. Sci. Technol.* **2012**, *46* (11), 5688−5695.

(3) Heath, G. A.; O'Donoughue, P.; Arent, D. J.; Bazilian, M. Harmonization of initial estimates of shale gas life cycle greenhouse gas emissions for electric power generation. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111* (31), E3167−E3176.

(4) IPCC *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.*; Cambridge University Press: Cambridge, 2013; p 1535.

(5) Alvarez, R. A.; Pacala, S. W.; Winebrake, J. J.; Chameides, W. L.; Hamburg, S. P. Greater focus needed on methane leakage from natural gas infrastructure. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109* (17), 6435−6440.

(6) Howarth, R. W.; Santoro, R.; Ingraffea, A. Methane and the greenhouse-gas footprint of natural gas from shale formations. *Climatic Change* **2011**, *106* (4), 679−690.

(7) Law, K. S.; Nisbet, E. G. Sensitivity of the CH_4 growth rate to changes in CH_4 emissions from natural gas and coal. *J. Geophys. Res.: Atmos.* **1996**, *101* (D9), 14387−14397.

(8) Dlugokencky, E. J.; Nisbet, E. G.; Fisher, R.; Lowry, D. Global atmospheric methane: Budget, changes, and dangers. *Philos. Trans. R. Soc., A* **2011**, *369* (1943), 2058−2072.

(9) Nisbet, E. G.; Dlugokencky, E. J.; Bousquet, P. Methane on the rise—Again. *Science* **2014**, *343* (6170), 493−495.

(10) Peischl, J.; Ryerson, T. B.; Aikin, K. C.; de Gouw, J. A.; Gilman, J. B.; Holloway, J. S.; Lerner, B. M.; Nadkarni, R.; Neuman, J. A.; Nowak, J. B.; et al. Quantifying atmospheric methane emissions from the Haynesville, Fayetteville, and northeastern Marcellus shale gas production regions. *J. Geophys. Res.: Atmos.* **2015**, *120* (5), 2119−2139.

(11) Kort, E. A.; Frankenberg, C.; Costigan, K. R.; Lindenmaier, R.; Dubey, M. K.; Wunch, D. Four Corners: The largest U.S. methane anomaly viewed from space. *Geophys. Res. Lett.* **2014**, *41* (19), 6898−6903.

(12) Pétron, G.; Frost, G.; Miller, B. R.; Hirsch, A. I.; Montzka, S. A.; Karion, A.; Trainer, M.; Sweeney, C.; Andrews, A. E.; Miller, L., et al., Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study. *J. Geophys. Res.: Atmos.* **2012**, *117*; 10.1029/2011jd016360.

(13) Karion, A.; Sweeney, C.; Pétron, G.; Frost, G.; Michael Hardesty, R.; Kofler, J.; Miller, B. R.; Newberger, T.; Wolter, S.; Banta, R.; et al. Methane emissions estimate from airborne measurements over a western United States natural gas field. *Geophys. Res. Lett.* **2013**, *40* (16), 4393−4397.

(14) Peischl, J.; Ryerson, T. B.; Brioude, J.; Aikin, K. C.; Andrews, A. E.; Atlas, E.; Blake, D.; Daube, B. C.; de Gouw, J. A.; Dlugokencky, E.; et al. Quantifying sources of methane using light alkanes in the Los Angeles basin, California. *J. Geophys. Res.: Atmos.* **2013**, *118* (10), 4974−4990.

(15) Wennberg, P. O.; Mui, W.; Wunch, D.; Kort, E. A.; Blake, D. R.; Atlas, E. L.; Santoni, G. W.; Wofsy, S. C.; Diskin, G. S.; Jeong, S.; et al. On the sources of methane to the Los Angeles atmosphere. *Environ. Sci. Technol.* **2012**, *46* (17), 9282−9289.

(16) Pétron, G.; Karion, A.; Sweeney, C.; Miller, B. R.; Montzka, S. A.; Frost, G.; Trainer, M.; Tans, P.; Andrews, A.; Kofler, J.; et al. A new look at methane and non-methane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver−Julesburg Basin. *J. Geophys. Res.: Atmos.* **2014**, *119* (11), 6836−6852.

(17) Caulton, D. R.; Shepson, P. B.; Santoro, R. L.; Sparks, J. P.; Howarth, R. W.; Ingraffea, A. R.; Cambaliza, M. O. L.; Sweeney, C.; Karion, A.; Davis, K. J.; et al. Toward a better understanding and quantification of methane emissions from shale gas development. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111* (17), 6237−6242.

(18) Schwietzke, S.; Griffin, W. M.; Matthews, H. S.; Bruhwiler, L. M. P. Natural gas fugitive emissions rates constrained by global atmospheric methane and ethane. *Environ. Sci. Technol.* **2014**, *48* (14), 7714−7722.

(19) Kort, E. A.; Eluszkiewicz, J.; Stephens, B. B.; Miller, J. B.; Gerbig, C.; Nehrkorn, T.; Daube, B. C.; Kaplan, J. O.; Houweling, S.; Wofsy, S. C. Emissions of CH_4 and N_2O over the United States and Canada based on a receptor-oriented modeling framework and COBRA-NA atmospheric observations. *Geophys. Res. Lett.* **2008**, *35* (18), 5.

(20) Katzenstein, A. S.; Doezema, L. A.; Simpson, I. J.; Blake, D. R.; Rowland, F. S. Extensive regional atmospheric hydrocarbon pollution in the southwestern United States. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100* (21), 11975−11979.

(21) Miller, S. M.; Wofsy, S. C.; Michalak, A. M.; Kort, E. A.; Andrews, A. E.; Biraud, S. C.; Dlugokencky, E. J.; Eluszkiewicz, J.; Fischer, M. L.; Janssens-Maenhout, G.; et al. Anthropogenic emissions of methane in the United States. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 20018−20022.

(22) McKain, K.; Down, A.; Raciti, S. M.; Budney, J.; Hutyra, L. R.; Floerchinger, C.; Herndon, S. C.; Nehrkorn, T.; Zahniser, M. S.; Jackson, R. B.; et al. Methane emissions from natural gas infrastructure and use in the urban region of Boston, Massachusetts. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112* (7), 1941−1946.

(23) Phillips, N. G.; Ackley, R.; Crosson, E. R.; Down, A.; Hutyra, L. R.; Brondfield, M.; Karr, J. D.; Zhao, K.; Jackson, R. B. Mapping urban pipeline leaks: Methane leaks across Boston. *Environ. Pollut.* **2013**, *173*, 1−4.

(24) Jackson, R. B.; Down, A.; Phillips, N. G.; Ackley, R. C.; Cook, C. W.; Plata, D. L.; Zhao, K. Natural Gas Pipeline Leaks Across Washington, DC. *Environ. Sci. Technol.* **2014**, *48* (3), 2051−2058.

(25) *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990−2011*; EPA: Washington, DC, 2013.

(26) European Commission Joint Research Centre (JRC)/Netherlands Environmental Assessment Agency (PBL), *Emission Database for Global Atmospheric Research (EDGAR)*, release version 4.2. http://edgar.jrc.ec.europa.eu. 2010.

(27) Brandt, A. R.; Heath, G. A.; Kort, E. A.; O'Sullivan, F.; Pétron, G.; Jordaan, S. M.; Tans, P.; Wilcox, J.; Gopstein, A. M.; Arent, D.; et al. Methane Leaks from North American Natural Gas Systems. *Science* **2014**, *343* (6172), 733−735.

(28) Allen, D. T.; Torres, V. M.; Thomas, J.; Sullivan, D. W.; Harrison, M.; Hendler, A.; Herndon, S. C.; Kolb, C. E.; Fraser, M. P.; Hill, A. D.; et al. Measurements of methane emissions at natural gas

DOI: 10.1021/acs.est.5b00217
Environ. Sci. Technol. 2015, 49, 8124−8131

production sites in the United States. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110* (44), 17768−17773.
(29) Texas Railroad Commission http://webapps.rrc.state.tx.us/PDQ/generalReportAction.do (accessed Oct 21, 2014).
(30) U.S. Department of Energy *Energy Information Administration Natural Gas Gross Withdrawals and Production*. http://www.eia.gov/dnav/ng/ng_prod_sum_dcu_NUS_m.htm (accessed Aug 27, 2014).
(31) Texas Railroad Commission http://www.rrc.state.tx.us/oil-gas/major-oil-gas-formations/barnett-shale-information/ (accessed Sept 29, 2014).
(32) Rich, A.; Grover, J. P.; Sattler, M. L. An exploratory study of air emissions associated with shale gas development and production in the Barnett Shale. *J. Air Waste Manage. Assoc.* **2014**, *64* (1), 61−72.
(33) Eapi, G. R.; Sabnis, M. S.; Sattler, M. L. Mobile measurement of methane and hydrogen sulfide at natural gas production site fence lines in the Texas Barnett Shale. *J. Air Waste Manage. Assoc.* **2014**, *64* (8), 927−944.
(34) Heath, G.; Meldrum, J.; Fisher, N.; Arent, D.; Bazilian, M. Life cycle greenhouse gas emissions from Barnett Shale gas used to generate electricity. *Journal of Unconventional Oil and Gas Resources* **2014**.
(35) Bunch, A. G.; Perry, C. S.; Abraham, L.; Wikoff, D. S.; Tachovsky, J. A.; Hixon, J. G.; Urban, J. D.; Harris, M. A.; Haws, L. C. Evaluation of impact of shale gas operations in the Barnett Shale region on volatile organic compounds in air and potential human health risks. *Science of The Total Environment* **2014**, *468−469* (0), 832−842.
(36) Zavala-Araiza, D.; Sullivan, D. W.; Allen, D. T. Atmospheric hydrocarbon emissions and concentrations in the Barnett Shale natural gas production region. *Environ. Sci. Technol.* **2014**, *48* (9), 5314−5321.
(37) Smith, M. L.; Kort, E. A.; Karion, A.; Sweeney, C.; Herndon, S. C.; Yacovitch, T. I. Airborne ethane observations in the Barnett Shale: Quantification of ethane flux and attribution of methane emissions, DOI: 10.1021/acs.est.5b00219.
(38) Lyon, D.; Zavala-Araiza, D.; Alvarez, R.; Harriss, R.; Palacios, V.; Lan, X.; Talbot, R.; Lavoie, T.; Shepson, P.; Yacovitch, T.Using multi-scale measurements to improve methane emissions estimates from oil and gas operations in the Barnett Shale, Texas: A spatially-resolved emission inventory, DOI: 10.1021/es506359c.
(39) Yacovitch, T. I.; Herndon, S. C.; Roscioli, J. R.; Floerchinger, C.; McGovern, R. M.; Agnese, M.; Pétron, G.; Kofler, J.; Sweeney, C.; Karion, A.; et al. Demonstration of an Ethane Spectrometer for Methane Source Identification. *Environ. Sci. Technol.* **2014**, *48* (14), 8028−8034.
(40) U.S. Environmental Protection Agency *Greenhouse Gas Reporting Program*. http://www.epa.gov/ghgreporting/index.html (accessed Nov 13, 2014).
(41) Drilling Info, Inc., DI Desktop. 2014.
(42) Lauvaux, T.; Miles, N. L.; Richardson, S. J.; Deng, A.; Stauffer, D. R.; Davis, K. J.; Jacobson, G.; Rella, C.; Calonder, G.-P.; DeCola, P. L. Urban emissions of CO_2 from Davos, Switzerland: The first real-time monitoring system using an atmospheric inversion technique. *J. Appl. Meteorology and Climatology* **2013**, *52* (12), 2654−2668.
(43) Lauvaux, T.; Deng, A.; Gaudet, B.; Sweeney, C.; Petron, G.; Karion, A.; Brewer, A.; Hardesty, M.; Herndon, S.; Yacovitch, T., et al. *Quantification of methane sources in the Barnett Shale (Texas) using the Penn State WRF-Chem-FDDA realtime modeling system*, In Proceedings of the 14th WRF User's Workshop, Boulder, CO, June 24−28, 2013; National Center for Atmospheric Research (NCAR): Boulder, CO, 2013 (http://www2.mmm.ucar.edu/wrf/users/workshops/WS2013/extended_abstracts/p20.pdf).
(44) Deng, A.; Stauffer, D.; Gaudet, B.; Dudhia, J.; Hacker, J.; Bruyere, C.; Wu, W.; Vandenberghe, F.; Liu, Y.; Bourgeois, A.*Update on WRF-ARW end-to-end multi-scale FDDA system*, In Proceedings of the 10th Annual WRF Users' Workshop, Boulder, CO, June 23−26, 2009; National Center for Atmospheric Research (NCAR): Boulder, CO, 2009 (http://www2.mmm.ucar.edu/wrf/users/workshops/WS2009/abstracts/1-09.pdf).

DOI: 10.1021/acs.est.5b00217
Environ. Sci. Technol. 2015, 49, 8124−8131